BEAD FILLER RUBBER COMPOSITION

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Abstract of **JP 55054337 (A)**
PURPOSE:An extremely hard rubber composition usable for bead filler rubber, having improved rigidity and durability, comprising a (modified) novolak phenolic resin and carbon black. CONSTITUTION:A composion comprising (A) 100 parts by wt. of natural polyisoprene, polybutadiene, or styrene-butadiene copolymer rubber, or their blend, (B) 40-170 parts by wt., preferably 60-120 parts by wt., of carbon black having a dibutyl phthalate absrption <=130ml/100g and an iodine adsorption of 40-130mg/g, (C) 15-45 parts by wt., preferably 20-40 parts by wt. based on 100 parts by wt., of (B) of a (modified) novolak phenolic resin, and (D) a curing agent, e.g. hexamethylenetetramine. The use of a movolak phenolic resin and its modified one at a weight ratio of 80:20-20:80 improves the durability synergistically.

United States Patent [19]

Miyake et al.

[11] 4,421,891

[45] Dec. 20, 1983

[54] BEAD FILLER RUBBER COMPOSITION

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[63] Continuation of Ser. No. 85,346, Oct. 16, 1979, abandoned.

[30] **Foreign Application Priority Data**

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[52] U.S. Cl. .... 524/495; 152/362 R; 524/511; 524/575.1; 525/139; 260/727; 260/775; 260/779 R

[58] Field of Search .... 524/495, 511; 525/139; 152/362 R; 260/727, 775, 779 R

[56] **References Cited**

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Attorney, Agent, or Firm—Sughrue, Mion, Zinn, Macpeak, and Seas

[57] **ABSTRACT**

A rubber composition comprising rubber, novolak-type phenolic resin and carbon black is very rigid and is adapted to be used as a bead filler rubber of a tire. Tires using the rubber composition are excellent in the high speed performance, lateral rigidity, ride feeling and durability.

8 Claims, 2 Drawing Figures

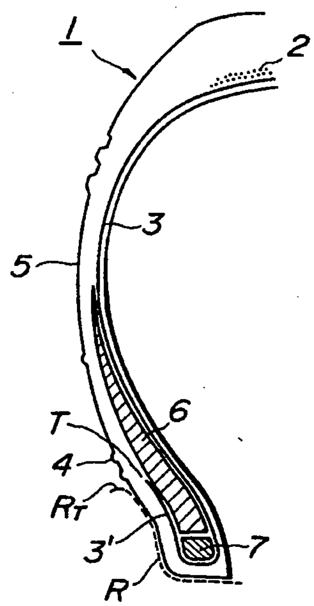


FIG. 1

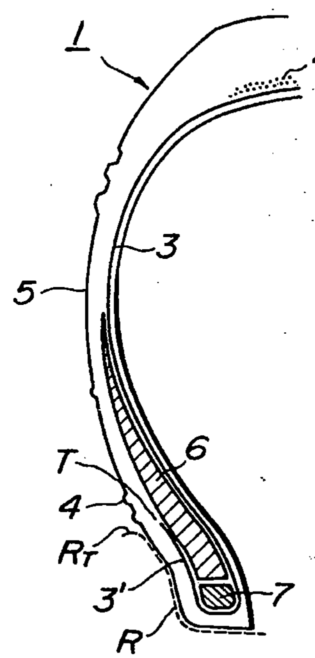
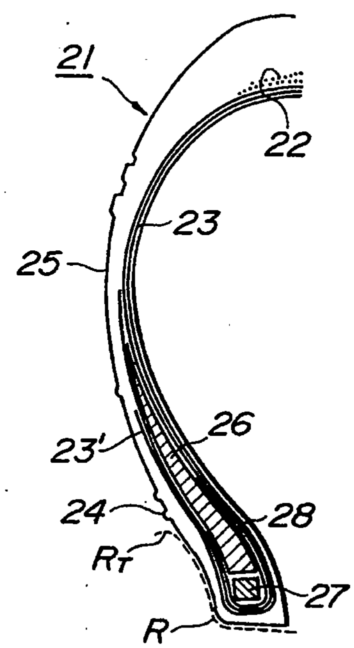


FIG. 2



BEAD FILLER RUBBER COMPOSITION

This is a continuation of application Ser. No. 85,346, filed Oct. 16, 1979, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a rubber composition, and more particularly, relates to a super rigid rubber composition comprising rubber, novolak-type phenolic resin and carbon black, and adapted to be used as a bead filler rubber of a tire.

2. Description of the Prior Art

There have been variously investigated the structure of bead portion of radial tire in order to satisfy the rigidity and durability required to tire. For example, it has been attempted to improve the dynamic performance and durability of tire by arranging a bead-reinforcing layer in the bead portion. However, this method has drawbacks that a large number of production steps are necessary and the productivity of the tire is very poor.

Japanese Utility Model Application No. 16,084/72, French Patent No. 1,260,138 and U.S. Pat. No. 4,067,373 disclose methods for improving the running performance and other property by arranging super rigid rubber in the bead portion. However, these methods do not substantially think of rubber, which can develop fully a function as a bead filler rubber subjected to complicated forces during the running of a tire and can give a sufficiently high durability to a rubber tire.

While, it is well known to use novolak-type phenolic resin in the production of rigid rubber compositions. However, these rubber compositions substantially concern nitrile rubber and neoprene rubber having a high compatibility with the resin. The nitrile rubber series of neoprene rubber series rigid rubber is very difficult to be vulcanized together with natural rubber, polybutadiene rubber and the like, which are commonly used as a rubber for tire, and therefore when the nitrile rubber series or neoprene rubber series rigid rubber is used as a tire part, the rubber is apt to be separated from natural rubber, polybutadiene rubber or the like, and can not be practically used.

In order to solve the above described drawbacks, the inventors have variously investigated how to produce a super rigid rubber composition by compounding novolak-type phenolic resin to natural rubber, polybutadiene rubber or the like, and found out the following facts. Novolak-type phenolic resin is essentially incompatible with natural rubber and other rubbers. Therefore, novolak-type phenolic resin is formed into spherical agglomerates during the kneading commonly carried out in the production of rubber, and has the filling effect only. This phenomenon still occurs even when various resins are used as a resin in place of novolak-type phenolic resin for producing a homogenous mixture of the resin with the rubber. However, when novolak-type phenolic resin is compounded to natural rubber or other rubber together with carbon black, the mixture of the resin and carbon black exhibits a reinforcing effect on the rubber, which is completely different from the reinforcing effect of the resin alone on the rubber or the reinforcing effect of the carbon black alone on the rubber, depending upon the mixing ratio of the resin to the carbon black, and a super rigid rubber composition having a durability remarkably superior to that of conventional resin-reinforced rubber can be obtained. That is, when natural rubber or diene series rubber is mixed with novolak-type phenolic resin, which is essentially incompatible with the rubber, the resin is separated from the rubber to form island-like large agglomerates in the mixture, but when a mixture of novolak-type phenolic resin and carbon black is compounded to natural rubber or other diene series rubber, the resin disperses uniformly in the rubber without forming large agglomerates similarly to the dispersed state in an ordinary mixture of rubber and carbon black. This action of carbon black to the resin is highly influenced by the mixing ratio of the carbon black to the resin and by the kind of the carbon black. Based on the discovery, the inventors have accomplished the present invention.

SUMMARY OF THE INVENTION

The feature of the present invention is the provision of a bead filler rubber composition, comprising 100 parts by weight of a rubber selected from the group consisting of natural rubber, polyisoprene rubber, polybutadiene rubber, styrene-butadiene copolymer rubber and blends thereof, 40–130 parts by weight of carbon black, 15–45 parts by weight based on 100 parts by weight of the carbon black of at least one of novolak-type phenolic resin and novolak-type modified phenolic resin, and a hardener for the resin.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of the side portion of a tire according to the present invention; and

FIG. 2 is a cross-sectional view of the side portion of a conventional tire.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The rubber to be used in the present invention includes natural rubber, polyisoprene rubber, polybutadiene rubber, styrene-butadiene copolymer rubber and blends thereof. Carbon black is compounded to the rubber in an amount of 40–130 parts by weight, preferably 60–120 parts by weight, more preferably 65–85 parts by weight, based on 100 parts by weight of the rubber. The use of carbon black in an amount of less than 40 parts by weight is too small to disperse homogeneously the necessary amount of resin for reinforcing the rubber. While, when the amount of carbon black is more than 130 parts by weight, the resulting rubber composition is brittle and is very poor in the durability. Further, in the present invention, carbon black having an iodine adsorbability (IA) of 40–130 mg/g and a dibutyl phthalate absorbability (DBP) of not more than 130 ml/100 g defined in ASTM D 1765 is preferably used. Carbon black having an IA of less than 40 mg/g affects adversely the dispersibility of the resin, and carbon black having an IA of more than 130 mg/g is poor in the dispersibility in itself. Therefore, the use of such carbon black is not preferable. When carbon black has a DBP of more then 130 ml/100 g, the carbon black used in an amount sufficient to disperse the resin can not be fully dispersed in the rubber.

In the present invention, the above described carbon black is used together with at least one of novolak-type phenolic resin and novolak-type modified phenolic resin. The novolak-type phenolic resin includes novolak-type phenol resin, novolak-type cresol resin and novolak-type resorcinol resin. The novolak-type modified phenolic resin includes resins obtained by modify-

ing the above described novolak-type phenolic resin with oils, such as rosin oil, tall oil, cashew nut oil, linoleic acid, oleic acid, linolenic acid and the like; resins obtained by modifying the novolak-type phenolic resin with aromatic hydrocarbons, such as xylene, mesitylene and the like; resins obtained by modifying the novolak-type phenolic resin with rubbers, such as nitrile rubber and the like. These resins are added to the rubber in an amount of 15–45 parts by weight, preferably 20–40 parts by weight, based on 100 parts by weight of carbon black. When the amount of resin is less than 15 parts by weight, the effect of the resin does not substantially appear, while when the amount of resin exceeds 45 parts by weight, excess resin forms agglomerates to cause phase separation in the resulting rubber composition, and deteriorates noticeably the physical properties of the rubber composition.

Further, in the present invention, a mixture of the novolak-type phenolic resin and the novolak-type modified phenolic resin is preferably used, because the use of the mixture can improve synergistically the durability of the resulting rubber composition as compared with the case where these resins are used alone. In this case, the mixing ratio of novolak-type phenolic resin to novolak-type modified phenolic resin, particularly the mixing ratio of novolak-type phenol resin to novolak-type cashew modified phenol resin or to novolak-type tall oil modified phenol resin, shoud be 80/20-20/80, preferably 60/40-40/60.

In the present invention, as the hardener for the resin, aldehyde-donors, that is, aldehyde-generating agents, such as hexamethylenetetramine, paraformaldehyde, hexamethoxymethylmelamine and the like, are preferably used. The hardener is used in an amount enough to harden the resin.

In the present invention, in addition to the above described ingredients, vulcanizing agents, such as sulfur, N,N'-dithiodiamines, thiurums and the like, vulcanization accelerator, antioxidant, fillers other than carbon black, such as silica and the like, process oil and other additives may be contained in the rubber composition.

The following examples are given for the purpose of illustration of this invention and are not intended as limitations thereof.

EXAMPLE 1

Homogeneous rubber compositions having a compounding recipe (parts by weight) shown in the following Table 1 were vulcanized at 145° C. for 40 minutes in a press to produce vulcanized rubber sheets having a thickness of 2 mm. The elongation at break (Eb), 20% modulus and dynamic modulus of the rubber sheets are shown in Table 1. The elongation at break and 20% modulus were measured with respect to an ASTM F type dumbbell according to ASTM D 412. The dynamic modulus was measured at room temperature with respect to a strip-shaped sample having a length of 25 mm, a width of 5 mm and a thickness of 2 mm by means of a high-power spectrometer made by Iwamoto Seisakusho by vibrating the sample at a frequency of 10 Hz and under a dynamic strain of 2%, the sample being used under an elongated state of 5% obtained by applying a static pressure.

It can be seen from Table 1 that a rubber composition containing resin and carbon black in a mixing ratio defined in the present invention has remarkably improved 20% modulus and dynamic modulus, and further has a satisfactorily high elongation at break for practical use.

In order to make a tire light in weight and to improve the ride feeling thereof, provision was made of a tire 1 shown in FIG. 1, which had a size of 165 SR 13 and comprised a belt layer 2 composed of two steel cord plies and a carcass layer 3 composed of one ply formed of polyethylene terephthalate fiber of 1500 d/2 and a bead filler 6, the carcass ply having a turn-up portion 3' extending up to a low position near a rim flange R_T. In FIG. 1, the numeral 4 represents a bead portion, the numeral 5 represents a side wall portion, the numeral 7 represents a bead wire, and the letter R represents a rim. Rubber composition No. 1, No. 3, No. 5, No. 7 and No. 8 shown in Table 1 were used as a rubber for the bead filler 6 of the tire shown in FIG. 1, and the high speed performance, lateral rigidity index, ride feeling and durability (condition A) of the tire were evaluated. The obtained results are shown in the following Table 2.

For comparison, rubber composition No. 1 (conventional rubber composition) described in Table 1 was used as a rubber for the bead filler 26 of a conventional tire 21 shown in FIG. 2, which had a structure that the turn-up portion 23' of a carcass ply extended up to the vicinity of the maximum width portion of the side wall portion 25. In FIG. 2, the numeral 22 represents a belt layer, the numeral 23 represents a carcass layer, the numeral 24 represents a bead portion, the numeral 27 represents a bead wire, the numeral 28 represents a cord layer, the letter R represents a rim and the letter R_T represents a rim flange. The high speed performance, lateral rigidity index, ride feeling and durability (condition A) of the tire 21 using Rubber composition No. 1 were evaluated. The obtained results are also shown in Table 2.

The evaluation of the performances was carried out in the following manner.

(1) High speed performance:

A tire is assembled in a 4½ J rim, inflated under an internal pressure of 2.1 kg/cm^2 and pressed on a drum having a diameter of 1.7 m under a load of 390 kg/cm^2. The tire is run on the drum at a speed of 80 km/hr for 2 hours and left to stand for 3 hours. Then, the tire is run at a speed of 121 km/hr for 30 minutes. When the tire runs without trouble, the speed is raised stepwise by 8 km/hr every 30 minutes. The high speed performance of the tire is evaluated by the speed at the breakage of the tire and by the running time until the breakage at the speed.

(2) Lateral rigidity index:

A tire is assembled in a 4½ J rim and inflated under an internal pressure of 1.7 kg/cm^2. The tire is pressed and fixed to a push car, which has a jagged non-slip surface, under a vertical load of 320 kg, the push car is pulled in a direction perpendicular to the direction of the tire, and the lateral road, which is caused at a lateral shift of the tire of 15 mm, is measured. The lateral rigidity index of a sample tire is indicated by the ratio of the lateral road of the sample tire to that, calculated as 100, of Conventional tire A.

(3) Ride feeling:

The ride feelings of the above obtained tires were compared with each other by the impact index and damping index measured in the following manner.

A tire is travelled at a speed of 50 km/hr on a road having rubber projections of 10 mm height fixed thereto, and the vibration subjected to the tire in the up-and-down direction is measured in the form of a

reaction in the rotating shaft of the tire by means of an acceleration meter. The impact absorbing property of a sample tire is indicated by the impact index, which is the reciprocal of the ratio of the amplitude in the first period of the above measured wave shape in the tire to that, calculaed as 100, in Conventional tire A.

The vibration damping property of a sample tire is indicated by the damping index, which is the recprocal of the ratio of the damping coefficient calculated from the above measured wave shape in the tire to that, calculated as 100, in Conventional tire A.

(4) Durability (condition A):

A tire is assembled in a $4\frac{1}{2}$ J rim, and pressed on a metal drum having a diameter of 1.7 m under an overload and over internal pressure condition that the strain energy concentrated to the turn-up end of the carcass ply is as large as about 4 times of the strain energy in a practically running tire. Then, the tire is run at a speed of 60 km/hr, and the durability of the tire is shown by the running distance until breakage occurs at the turn-up end of carcass ply. When the running distance of a tire without trouble is over 30,000 km, the tire is evaluated as an acceptable tire.

TABLE 1

Rubber composition No.	1	2	3	4	5	6	7	8	9	10
Compounding recipe (parts by weight)										
Natural rubber	100	100	100	100	100	100	100	100	50	50
Styrene-butadiene copolymer rubber									50	
Polybutadiene rubber										50
Carbon black*	70		70	70	70	70	70	100	70	70
Novalak-type cashew modified phenol resin**		20	8	14	20	26	40	30	20	20
Stearic acid	2	2	2	2	2	2	2	2	2	2
Zinc white	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5
N—oxydiethylenebenzothiazole sulfeneamide	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulfur	4	4	4	4	4	4	4	4	4	4
Hexamethylenetetramine		2	0.8	1.4	2.0	2.6	4.0	3.0	2.0	2.0
Property										
Elongation at break (%)	170	380	220	230	225	200	100	145	220	190
20% modulus (kg/cm^2)	13.5	7.5	35.0	43.0	60.5	69.0	92.0	89.0	55.0	63.5
Dynamic modulus (kg/cm^2)	120	40	350	520	730	890	1,530	1,420	710	775

*IA:82 mg/g. DBP:102 ml/100 g

**Novolak-type phenol resin obtained by modifying 100 parts by weight of phenol with 40 parts by weight of cashoew nut oil

TABLE 2

Tire	A	B	C	D	E	F
Tire structure	FIG. 2	FIG. 1	FIG. 1	FIG. 1	FIG. 1	FIG. 1
Rubber composition used in bead filler	No. 1	No. 1	No. 3	No. 5	No. 7	No. 8
Performance						
High-speed performance						
Speed (km/h)	185	169	177	185	193	193
Running time (min)	23	28	27	28	2	4
Lateral rigidity index	100	75	93	103	112	110
Ride feeling						
Impact index	100	115	112	109	105	106
Damping index	100	86	93	110	115	113
Durability (condition A)	run over 30,000 km	11,000 km	21,500 km	run over 30,000 km	16,500 km	run over 30,000 km

It can be seen from Table 2 that, when the rubber composition of the present invention is used as a bead filler rubber of a tire, the tire has equal or superior to Conventional tire A in the high speed performance, cornering stability and durability and further is remarkably superior to Conventional tire A in the ride feeling.

EXAMPLE 2

Rubber compositions were produced in the same compounding recipe as that of Rubber composition No. 5 in Table 1, except that only the carbon black is replaced by carbon blacks shown in the following Table 3. The viscosity of the resulting rubber compositions was measured according to JIS K 6300, and the elongation at break, 20% modulus and dynamic modulus thereof were measured in the same manner as described in Example 1. Then, tires having a structure shown in FIG. 1 were produced by the use of the rubber compositions, and the performances of the tires were evaluated in the same manner as described in Example 1. The obtained results are shown in Table 3.

TABLE 3

Rubber Composition No.	11	12	13	5	15	16	17
Carbon black							
IA (mg/g)	36	43	86	82	84	121	145
DBP (ml/100 g)	91	121	60	102	150	114	113
Property							
Mooney viscosity	66	73	85	92	125	105	132
Elongation at break (%)	200	220	250	225	200	210	190
20% modulus (kg/cm^2)	38.5	50.5	51.5	60.5	45.0	53.0	42.5

TABLE 3-continued

Dynamic modulus (kg/cm²)	420	610	625	750	595	715	530
Tire	G	H	I	D		J	
Performance							
High-speed performance							
Speed (km/hr)	185	185	185	185		185	
running time (min)	10	21	20	28		20	
Lateral rigidity index	95	97	97	103		98	
Durability (condition A)	18,000 km	run over 30,000 km	run over 30,000 km	run over 30,000 km		run over 30,000 km	

It can be seen from Table 3 that tires having more improved durability can be obtained by the use of carbon black having an IA of 40–130 mg/g and a DBP of not higher than 130 ml/100 g. Rubber composition No. 15 and No. 17 are very poor in the fluidity in the unvulcanized state, and are very difficult in the extrusion-molding. Therefore, the evaluation of tires using the rubber compositions are omitted.

EXAMPLE 3

Rubber compositions were produced according to the compounding recipe shown in the following Table 4. The fatigue life of the rubber compositions was measured in the method as explained later, and other properties thereof were measured in the same manner as described in Example 1. The obtained results are shown in Table 4.

The fatigue life of the rubber composition was measured in the following manner according to ASTM D 412. That is, an ASTM F type dumbbell of the rubber composition was fixed under an elongated state of 35% and vibrated at 170° C. by means of an elongation type fatigue tester, and the number of vibrations until the durmbbell was broken was measured.

Then, tires having a structure shown in FIG. 1 were produced by the use of Rubber composition Nos. 22–26 shown in Table 4, and the performance of the tires was evaluated in the same manner as described in Example 1. In this case, the durability of the tires was evaluated, not only under condition A, but also under a more severe condition (condition B), that is, under a super overload and super over internal pressure condition, wherein strain energy concentrated to the turn-up end of carcass ply is as large as 8 times of the strain energy in a practically running tire. The obtained results are shown in Table 5.

It can be seen from Tables 4 and 5 that, when unmodified phenolic resin is used together with modified phenolic resin, the resulting rubber composition has a synergistically improved durability.

TABLE 4

Rubber Composition No.	18	19	20	21	22	23	24	25	26
Compounding recipe (parts by weight)									
Natural rubber	100	100	100	100	100	100	100	100	100
Carbon black*	75	75	75	75	75	75	75	75	75
Cashew-modified phenol resin**	24	18	18	6					
Phenol resin***		6	12	18	24	18	12	6	
Tall oil-modified phenol resin****						6	12	18	24
Stearic acid	2	2	2	2	2	2	2	2	2
Zinc white	10	10	10	10	10	10	10	10	10
N—oxydiethylenebenzothiazole sulfeneamide	1	1	1	1	1	1	1	1	1
Sulfur	6	6	6	6	6	6	6	6	6
Hexamethylenetetramine	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
Property									
Elongation at break (%)	160	160	155	140	120	145	170	165	160
20% modulus (kg/cm²)	72	70	67	58	52	58	65	66	67
Dynamic modulus (kg/cm²)	980	920	890	715	650	710	780	840	880
Fatigue life (number of vibrations)	2×10^6	3×10^6	5×10^6	4×10^6	3×10^6	6×10^6	8×10^6	4×10^6	1×10^6

*IA:82 mg/g, DBP:102 ml/100 g
**Novolak-type phenol resin obtained by modifying 100 parts by weight of phenol with 40 parts by weight of cashew nut oil
***Unmodified novolak-type phenol resin
****Novolak-type phenol resin obtained by modifying 100 parts by weight of phenol with 40 parts by weight of tall oil

TABLE 5

Tire	K	L	M	N	O
Rubber composition used in bead filler	No. 22	No. 23	No. 24	No. 25	No. 26
High speed performance					
Speed (km/h)	185	185	185	185	185
Running time (min)	12	21	28	27	28
Lateral rigidity index	98	101	105	106	106
Durability (condition A)	run over 30,000 km	run over 30,000 km	run over 30,000 km	run over 30,000 km	run over 30,000 km
Durability (condition B)	rubber is broken after 9,800 km running	run over 13,000 km	run over 13,000 km	run over 13,000 km	rubber is broken after 13,000 km running

What is claimed is:

1. A bead filler rubber composition, consisting essentially of:

(a) 100 parts by weight of a rubber selected from the group consisting of natural rubber, polyisoprene rubber, polybutadiene rubber, styrene-butadiene copolymer rubber and blends thereof;

(b) 40–130 parts by weight of carbon black having an iodine adsorbability of 40–130 mg/g and a dibutyl phthalate absorbability of not higher than 130 ml/100 g;

(c) 15–45 parts by weight per 100 parts by weight of carbon black of a mixture of a novolak phenolic resin selected from the group consisting of novolak phenol resin, novolak cresol resin, novolak resorcinol resin; and a novolak modified phenolic resin obtained by modifying with a compound selected from the group consisting of oils, aromatic hydrocarbons, or rubbers, wherein the mixing ratio of the novolak phenolic resin to the novolak modified phenolic resin is from 80/20 to 20/80 by weight, an effective amount of a hardener for the resin.

2. A bead filler rubber composition according to claim 1, wherein the amount of the carbon black is 60–120 parts by weight based on 100 parts by weight of the rubber.

3. A bead filler rubber composition according to claim 1, wherein the amount of the novolak-type phenolic resin is 20–40 parts by weight based on 100 parts by weight of the carbon black.

4. A bead filler rubber composition according to claim 1, wherein the mixing ratio of the novolak phenolic resin/the modified novolak phenolic resin is 60/40-40/60.

5. A bead filler rubber composition according to claim 1 wherein said novolak modified phenolic resins are novolak phenolic resins modified with an oil selected from the group consisting of rosin oil, tall oil and cashew nut oil.

6. A bead filler rubber composition according to claim 1, wherein said novolak modified phenolic resins are novolak phenolic resins modified with an oil selected from the group consisting of linoleic acid, oleic acid and linolenic acid.

7. A bead filler rubber composition according to claim 1, wherein said novolak modified phenolic resins are novolak phenolic resins modified with an aromatic hydrocarbon selected from the group consisting of xylene and mesitylene.

8. A bead filler rubber composition according to claim 1, wherein said novolak modified phenolic resins are novolak phenolic resins modified with a nitrile rubber.

* * * * *

United States Patent [19]

Miyake et al.

[11] **4,421,891**

[45] **Dec. 20, 1983**

[54] **BEAD FILLER RUBBER COMPOSITION**

[75] Inventors: **Itsuo Miyake**, Kodaira; **Keizo Okamoto**, Higashikurume; **Motonori Bundo**, Higashimurayama; **Akihiro Noda**, Kodaira, all of Japan

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Related U.S. Application Data

[63] Continuation of Ser. No. 85,346, Oct. 16, 1979, abandoned.

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[58] **Field of Search** .... 524/495, 511; 525/139; 152/362 R; 260/727, 775, 779 R

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[57] **ABSTRACT**

A rubber composition comprising rubber, novolak-type phenolic resin and carbon black is very rigid and is adapted to be used as a bead filler rubber of a tire. Tires using the rubber composition are excellent in the high speed performance, lateral rigidity, ride feeling and durability.

8 Claims, 2 Drawing Figures

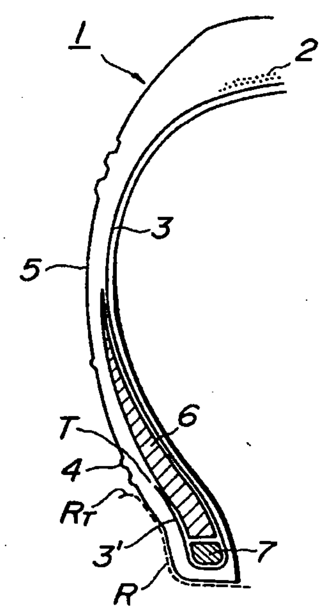


FIG. 1

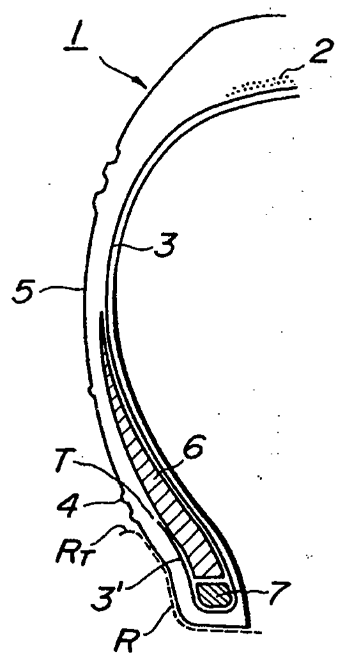
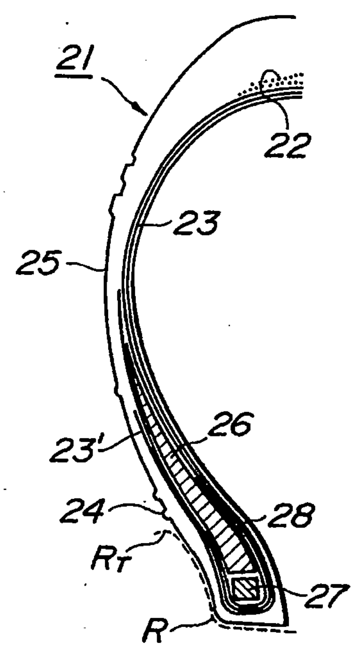


FIG. 2



BEAD FILLER RUBBER COMPOSITION

This is a continuation of application Ser. No. 85,346, filed Oct. 16, 1979, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a rubber composition, and more particularly, relates to a super rigid rubber composition comprising rubber, novolak-type phenolic resin and carbon black, and adapted to be used as a bead filler rubber of a tire.

2. Description of the Prior Art

There have been variously investigated the structure of bead portion of radial tire in order to satisfy the rigidity and durability required to tire. For example, it has been attempted to improve the dynamic performance and durability of tire by arranging a bead-reinforcing layer in the bead portion. However, this method has drawbacks that a large number of production steps are necessary and the productivity of the tire is very poor.

Japanese Utility Model Application No. 16,084/72, French Patent No. 1,260,138 and U.S. Pat. No. 4,067,373 disclose methods for improving the running performance and other property by arranging super rigid rubber in the bead portion. However, these methods do not substantially think of rubber, which can develop fully a function as a bead filler rubber subjected to complicated forces during the running of a tire and can give a sufficiently high durability to a rubber tire.

While, it is well known to use novolak-type phenolic resin in the production of rigid rubber compositions. However, these rubber compositions substantially concern nitrile rubber and neoprene rubber having a high compatibility with the resin. The nitrile rubber series of neoprene rubber series rigid rubber is very difficult to be vulcanized together with natural rubber, polybutadiene rubber and the like, which are commonly used as a rubber for tire, and therefore when the nitrile rubber series or neoprene rubber series rigid rubber is used as a tire part, the rubber is apt to be separated from natural rubber, polybutadiene rubber or the like, and can not be practically used.

In order to solve the above described drawbacks, the inventors have variously investigated how to produce a super rigid rubber composition by compounding novolak-type phenolic resin to natural rubber, polybutadiene rubber or the like, and found out the following facts. Novolak-type phenolic resin is essentially incompatible with natural rubber and other rubbers. Therefore, novolak-type phenolic resin is formed into spherical agglomerates during the kneading commonly carried out in the production of rubber, and has the filling effect only. This phenomenon still occurs even when various resins are used as a resin in place of novolak-type phenolic resin for producing a homogenous mixture of the resin with the rubber. However, when novolak-type phenolic resin is compounded to natural rubber or other rubber together with carbon black, the mixture of the resin and carbon black exhibits a reinforcing effect on the rubber, which is completely different from the reinforcing effect of the resin alone on the rubber or the reinforcing effect of the carbon black alone on the rubber, depending upon the mixing ratio of the resin to the carbon black, and a super rigid rubber composition having a durability remarkably superior to that of conventional resin-reinforced rubber can be obtained. That is, when natural rubber or diene series rubber is mixed with novolak-type phenolic resin, which is essentially incompatible with the rubber, the resin is separated from the rubber to form island-like large agglomerates in the mixture, but when a mixture of novolak-type phenolic resin and carbon black is compounded to natural rubber or other diene series rubber, the resin disperses uniformly in the rubber without forming large agglomerates similarly to the dispersed state in an ordinary mixture of rubber and carbon black. This action of carbon black to the resin is highly influenced by the mixing ratio of the carbon black to the resin and by the kind of the carbon black. Based on the discovery, the inventors have accomplished the present invention.

SUMMARY OF THE INVENTION

The feature of the present invention is the provision of a bead filler rubber composition, comprising 100 parts by weight of a rubber selected from the group consisting of natural rubber, polyisoprene rubber, polybutadiene rubber, styrene-butadiene copolymer rubber and blends thereof, 40–130 parts by weight of carbon black, 15–45 parts by weight based on 100 parts by weight of the carbon black of at least one of novolak-type phenolic resin and novolak-type modified phenolic resin, and a hardener for the resin.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of the side portion of a tire according to the present invention; and

FIG. 2 is a cross-sectional view of the side portion of a conventional tire.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The rubber to be used in the present invention includes natural rubber, polyisoprene rubber, polybutadiene rubber, styrene-butadiene copolymer rubber and blends thereof. Carbon black is compounded to the rubber in an amount of 40–130 parts by weight, preferably 60–120 parts by weight, more preferably 65–85 parts by weight, based on 100 parts by weight of the rubber. The use of carbon black in an amount of less than 40 parts by weight is too small to disperse homogeneously the necessary amount of resin for reinforcing the rubber. While, when the amount of carbon black is more than 130 parts by weight, the resulting rubber composition is brittle and is very poor in the durability. Further, in the present invention, carbon black having an iodine adsorbability (IA) of 40–130 mg/g and a dibutyl phthalate absorbability (DBP) of not more than 130 ml/100 g defined in ASTM D 1765 is preferably used. Carbon black having an IA of less than 40 mg/g affects adversely the dispersibility of the resin, and carbon black having an IA of more than 130 mg/g is poor in the dispersibility in itself. Therefore, the use of such carbon black is not preferable. When carbon black has a DBP of more then 130 ml/100 g, the carbon black used in an amount sufficient to disperse the resin can not be fully dispersed in the rubber.

In the present invention, the above described carbon black is used together with at least one of novolak-type phenolic resin and novolak-type modified phenolic resin. The novolak-type phenolic resin includes novolak-type phenol resin, novolak-type cresol resin and novolak-type resorcinol resin. The novolak-type modified phenolic resin includes resins obtained by modify-

ing the above described novolak-type phenolic resin with oils, such as rosin oil, tall oil, cashew nut oil, linoleic acid, oleic acid, linolenic acid and the like; resins obtained by modifying the novolak-type phenolic resin with aromatic hydrocarbons, such as xylene, mesitylene and the like; resins obtained by modifying the novolak-type phenolic resin with rubbers, such as nitrile rubber and the like. These resins are added to the rubber in an amount of 15–45 parts by weight, preferably 20–40 parts by weight, based on 100 parts by weight of carbon black. When the amount of resin is less than 15 parts by weight, the effect of the resin does not substantially appear, while when the amount of resin exceeds 45 parts by weight, excess resin forms agglomerates to cause phase separation in the resulting rubber composition, and deteriorates noticeably the physical properties of the rubber composition.

Further, in the present invention, a mixture of the novolak-type phenolic resin and the novolak-type modified phenolic resin is preferably used, because the use of the mixture can improve synergistically the durability of the resulting rubber composition as compared with the case where these resins are used alone. In this case, the mixing ratio of novolak-type phenolic resin to novolak-type modified phenolic resin, particularly the mixing ratio of novolak-type phenol resin to novolak-type cashew modified phenol resin or to novolak-type tall oil modified phenol resin, shoud be 80/20-20/80, preferably 60/40-40/60.

In the present invention, as the hardener for the resin, aldehyde-donors, that is, aldehyde-generating agents, such as hexamethylenetetramine, paraformaldehyde, hexamethoxymethylmelamine and the like, are preferably used. The hardener is used in an amount enough to harden the resin.

In the present invention, in addition to the above described ingredients, vulcanizing agents, such as sulfur, N,N'-dithiodiamines, thiurums and the like, vulcanization accelerator, antioxidant, fillers other than carbon black, such as silica and the like, process oil and other additives may be contained in the rubber composition.

The following examples are given for the purpose of illustration of this invention and are not intended as limitations thereof.

EXAMPLE 1

Homogeneous rubber compositions having a compounding recipe (parts by weight) shown in the following Table 1 were vulcanized at 145° C. for 40 minutes in a press to produce vulcanized rubber sheets having a thickness of 2 mm. The elongation at break (Eb), 20% modulus and dynamic modulus of the rubber sheets are shown in Table 1. The elongation at break and 20% modulus were measured with respect to an ASTM F type dumbbell according to ASTM D 412. The dynamic modulus was measured at room temperature with respect to a strip-shaped sample having a length of 25 mm, a width of 5 mm and a thickness of 2 mm by means of a high-power spectrometer made by Iwamoto Seisakusho by vibrating the sample at a frequency of 10 Hz and under a dynamic strain of 2%, the sample being used under an elongated state of 5% obtained by applying a static pressure.

It can be seen from Table 1 that a rubber composition containing resin and carbon black in a mixing ratio defined in the present invention has remarkably improved 20% modulus and dynamic modulus, and further has a satisfactorily high elongation at break for practical use.

In order to make a tire light in weight and to improve the ride feeling thereof, provision was made of a tire 1 shown in FIG. 1, which had a size of 165 SR 13 and comprised a belt layer 2 composed of two steel cord plies and a carcass layer 3 composed of one ply formed of polyethylene terephthalate fiber of 1500 d/2 and a bead filler 6, the carcass ply having a turn-up portion 3' extending up to a low position near a rim flange R_T. In FIG. 1, the numeral 4 represents a bead portion, the numeral 5 represents a side wall portion, the numeral 7 represents a bead wire, and the letter R represents a rim. Rubber composition No. 1, No. 3, No. 5, No. 7 and No. 8 shown in Table 1 were used as a rubber for the bead filler 6 of the tire shown in FIG. 1, and the high speed performance, lateral rigidity index, ride feeling and durability (condition A) of the tire were evaluated. The obtained results are shown in the following Table 2.

For comparison, rubber composition No. 1 (conventional rubber composition) described in Table 1 was used as a rubber for the bead filler 26 of a conventional tire 21 shown in FIG. 2, which had a structure that the turn-up portion 23' of a carcass ply extended up to the vicinity of the maximum width portion of the side wall portion 25. In FIG. 2, the numeral 22 represents a belt layer, the numeral 23 represents a carcass layer, the numeral 24 represents a bead portion, the numeral 27 represents a bead wire, the numeral 28 represents a cord layer, the letter R represents a rim and the letter R_T represents a rim flange. The high speed performance, lateral rigidity index, ride feeling and durability (condition A) of the tire 21 using Rubber composition No. 1 were evaluated. The obtained results are also shown in Table 2.

The evaluation of the performances was carried out in the following manner.

(1) High speed performance:

A tire is assembled in a 4½ J rim, inflated under an internal pressure of 2.1 kg/cm² and pressed on a drum having a diameter of 1.7 m under a load of 390 kg/cm². The tire is run on the drum at a speed of 80 km/hr for 2 hours and left to stand for 3 hours. Then, the tire is run at a speed of 121 km/hr for 30 minutes. When the tire runs without trouble, the speed is raised stepwise by 8 km/hr every 30 minutes. The high speed performance of the tire is evaluated by the speed at the breakage of the tire and by the running time until the breakage at the speed.

(2) Lateral rigidity index:

A tire is assembled in a 4½ J rim and inflated under an internal pressure of 1.7 kg/cm². The tire is pressed and fixed to a push car, which has a jagged non-slip surface, under a vertical load of 320 kg, the push car is pulled in a direction perpendicular to the direction of the tire, and the lateral road, which is caused at a lateral shift of the tire of 15 mm, is measured. The lateral rigidity index of a sample tire is indicated by the ratio of the lateral road of the sample tire to that, calculated as 100, of Conventional tire A.

(3) Ride feeling:

The ride feelings of the above obtained tires were compared with each other by the impact index and damping index measured in the following manner.

A tire is travelled at a speed of 50 km/hr on a road having rubber projections of 10 mm height fixed thereto, and the vibration subjected to the tire in the up-and-down direction is measured in the form of a

reaction in the rotating shaft of the tire by means of an acceleration meter. The impact absorbing property of a tire without trouble is over 30,000 km, the tire is evaluated as an acceptable tire.

TABLE 1

Rubber composition No.	1	2	3	4	5	6	7	8	9	10
Compounding recipe (parts by weight)										
Natural rubber	100	100	100	100	100	100	100	100	50	50
Styrene-butadiene copolymer rubber									50	
Polybutadiene rubber										50
Carbon black*	70		70	70	70	70	70	100	70	70
Novalak-type cashew modified phenol resin**		20	8	14	20	26	40	30	20	20
Stearic acid	2	2	2	2	2	2	2	2	2	2
Zinc white	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5
N—oxydiethylenebenzothiazole sulfeneamide	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulfur	4	4	4	4	4	4	4	4	4	4
Hexamethylenetetramine		2	0.8	1.4	2.0	2.6	4.0	3.0	2.0	2.0
Property										
Elongation at break (%)	170	380	220	230	225	200	100	145	220	190
20% modulus (kg/cm^2)	13.5	7.5	35.0	43.0	60.5	69.0	92.0	89.0	55.0	63.5
Dynamic modulus (kg/cm^2)	120	40	350	520	730	890	1,530	1,420	710	775

*IA:82 mg/g, DBP:102 ml/100 g
**Novolak-type phenol resin obtained by modifying 100 parts by weight of phenol with 40 parts by weight of cashoew nut oil

TABLE 2

Tire	A	B	C	D	E	F
Tire structure	FIG. 2	FIG. 1	FIG. 1	FIG. 1	FIG. 1	FIG. 1
Rubber composition used in bead filler	No. 1	No. 1	No. 3	No. 5	No. 7	No. 8
Performance						
High-speed performance						
Speed (km/h)	185	169	177	185	193	193
Running time (min)	23	28	27	28	2	4
Lateral rigidity index	100	75	93	103	112	110
Ride feeling						
Impact index	100	115	112	109	105	106
Damping index	100	86	93	110	115	113
Durability (condition A)	run over 30,000 km	11,000 km	21,500 km	run over 30,000 km	16,500 km	run over 30,000 km

sample tire is indicated by the impact index, which is the reciprocal of the ratio of the amplitude in the first period of the above measured wave shape in the tire to that, calculaed as 100, in Conventional tire A.

The vibration damping property of a sample tire is indicated by the damping index, which is the recproical of the ratio of the damping coefficient calculated from the above measured wave shape in the tire to that, calculated as 100, in Conventional tire A.

(4) Durability (condition A):

A tire is assembled in a $4\frac{1}{2}$ J rim, and pressed on a metal drum having a diameter of 1.7 m under an overload and over internal pressure condition that the strain energy concentrated to the turn-up end of the carcass ply is as large as about 4 times of the strain energy in a practically running tire. Then, the tire is run at a speed of 60 km/hr, and the durability of the tire is shown by the running distance until breakage occurs at the turn-up end of carcass ply. When the running distance of a

It can be seen from Table 2 that, when the rubber composition of the present invention is used as a bead filler rubber of a tire, the tire has equal or superior to Conventional tire A in the high speed performance, cornering stability and durability and further is remarkably superior to Conventional tire A in the ride feeling.

EXAMPLE 2

Rubber compositions were produced in the same compounding recipe as that of Rubber composition No. 5 in Table 1, except that only the carbon black is replaced by carbon blacks shown in the following Table 3. The viscosity of the resulting rubber compositions was measured according to JIS K 6300, and the elongation at break, 20% modulus and dynamic modulus thereof were measured in the same manner as described in Example 1. Then, tires having a structure shown in FIG. 1 were produced by the use of the rubber compositions, and the performances of the tires were evaluated in the same manner as described in Example 1. The obtained results are shown in Table 3.

TABLE 3

Rubber Composition No.	11	12	13	5	15	16	17
Carbon black							
IA (mg/g)	36	43	86	82	84	121	145
DBP (ml/100 g)	91	121	60	102	150	114	113
Property							
Mooney viscosity	66	73	85	92	125	105	132
Elongation at break (%)	200	220	250	225	200	210	190
20% modulus (kg/cm^2)	38.5	50.5	51.5	60.5	45.0	53.0	42.5

TABLE 3-continued

Dynamic modulus (kg/cm^2)	420	610	625	750	595	715	530
Tire	G	H	I	D		J	
Performance							
High-speed performance							
Speed (km/hr)	185	185	185	185		185	
running time (min)	10	21	20	28		20	
Lateral rigidity index	95	97	97	103		98	
Durability (condition A)	18,000 km	run over 30,000 km	run over 30,000 km	run over 30,000 km		run over 30,000 km	

It can be seen from Table 3 that tires having more improved durability can be obtained by the use of carbon black having an IA of 40–130 mg/g and a DBP of not higher than 130 ml/100 g. Rubber composition No. 15 and No. 17 are very poor in the fluidity in the unvulcanized state, and are very difficult in the extrusion-molding. Therefore, the evaluation of tires using the rubber compositions are omitted.

EXAMPLE 3

Rubber compositions were produced according to the compounding recipe shown in the following Table 4. The fatigue life of the rubber compositions was measured in the method as explained later, and other properties thereof were measured in the same manner as described in Example 1. The obtained results are shown in Table 4.

The fatigue life of the rubber composition was measured in the following manner according to ASTM D 412. That is, an ASTM F type dumbbell of the rubber composition was fixed under an elongated state of 35% and vibrated at 170° C. by means of an elongation type fatigue tester, and the number of vibrations until the durmbbell was broken was measured.

Then, tires having a structure shown in FIG. 1 were produced by the use of Rubber composition Nos. 22–26 shown in Table 4, and the performance of the tires was evaluated in the same manner as described in Example 1. In this case, the durability of the tires was evaluated, not only under condition A, but also under a more severe condition (condition B), that is, under a super overload and super over internal pressure condition, wherein strain energy concentrated to the turn-up end of carcass ply is as large as 8 times of the strain energy in a practically running tire. The obtained results are shown in Table 5.

It can be seen from Tables 4 and 5 that, when unmodified phenolic resin is used together with modified phenolic resin, the resulting rubber composition has a synergistically improved durability.

TABLE 4

Rubber Composition No.	18	19	20	21	22	23	24	25	26
Compounding recipe (parts by weight)									
Natural rubber	100	100	100	100	100	100	100	100	100
Carbon black*	75	75	75	75	75	75	75	75	75
Cashew-modified phenol resin**	24	18	18	6					
Phenol resin***		6	12	18	24	18	12	6	
Tall oil-modified phenol resin****						6	12	18	24
Stearic acid	2	2	2	2	2	2	2	2	2
Zinc white	10	10	10	10	10	10	10	10	10
N—oxydiethylenebenzothiazole sulfeneamide	1	1	1	1	1	1	1	1	1
Sulfur	6	6	6	6	6	6	6	6	6
Hexamethylenetetramine	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
Property									
Elongation at break (%)	160	160	155	140	120	145	170	165	160
20% modulus (kg/cm^2)	72	70	67	58	52	58	65	66	67
Dynamic modulus (kg/cm^2)	980	920	890	715	650	710	780	840	880
Fatigue life (number of vibrations)	2×10^6	3×10^6	5×10^6	4×10^6	3×10^6	6×10^6	8×10^6	4×10^6	1×10^6

*IA:82 mg/g, DBP:102 ml/100 g

**Novolak-type phenol resin obtained by modifying 100 parts by weight of phenol with 40 parts by weight of cashew nut oil

***Unmodified novolak-type phenol resin

****Novolak-type phenol resin obtained by modifying 100 parts by weight of phenol with 40 parts by weight of tall oil

TABLE 5

Tire	K	L	M	N	O
Rubber composition used in bead filler	No. 22	No. 23	No. 24	No. 25	No. 26
High speed performance					
Speed (km/h)	185	185	185	185	185
Running time (min)	12	21	28	27	28
Lateral rigidity index	98	101	105	106	106
Durability (condition A)	run over 30,000 km	run over 30,000 km	run over 30,000 km	run over 30,000 km	run over 30,000 km
Durability (condition B)	rubber is broken after 9,800 km running	run over 13,000 km	run over 13,000 km	run over 13,000 km	rubber is broken after 13,000 km running

What is claimed is:

1. A bead filler rubber composition, consisting essentially of:

(a) 100 parts by weight of a rubber selected from the group consisting of natural rubber, polyisoprene rubber, polybutadiene rubber, styrene-butadiene copolymer rubber and blends thereof;

(b) 40–130 parts by weight of carbon black having an iodine adsorbability of 40–130 mg/g and a dibutyl phthalate absorbability of not higher than 130 ml/100 g;

(c) 15–45 parts by weight per 100 parts by weight of carbon black of a mixture of a novolak phenolic resin selected from the group consisting of novolak phenol resin, novolak cresol resin, novolak resorcinol resin; and a novolak modified phenolic resin obtained by modifying with a compound selected from the group consisting of oils, aromatic hydrocarbons, or rubbers, wherein the mixing ratio of the novolak phenolic resin to the novolak modified phenolic resin is from 80/20 to 20/80 by weight, an effective amount of a hardener for the resin.

2. A bead filler rubber composition according to claim 1, wherein the amount of the carbon black is 60–120 parts by weight based on 100 parts by weight of the rubber.

3. A bead filler rubber composition according to claim 1, wherein the amount of the novolak-type phenolic resin is 20–40 parts by weight based on 100 parts by weight of the carbon black.

4. A bead filler rubber composition according to claim 1, wherein the mixing ratio of the novolak phenolic resin/the modified novolak phenolic resin is 60/40-40/60.

5. A bead filler rubber composition according to claim 1 wherein said novolak modified phenolic resins are novolak phenolic resins modified with an oil selected from the group consisting of rosin oil, tall oil and cashew nut oil.

6. A bead filler rubber composition according to claim 1, wherein said novolak modified phenolic resins are novolak phenolic resins modified with an oil selected from the group consisting of linoleic acid, oleic acid and linolenic acid.

7. A bead filler rubber composition according to claim 1, wherein said novolak modified phenolic resins are novolak phenolic resins modified with an aromatic hydrocarbon selected from the group consisting of xylene and mesitylene.

8. A bead filler rubber composition according to claim 1, wherein said novolak modified phenolic resins are novolak phenolic resins modified with a nitrile rubber.

* * * * *

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C 08 K 3／04	CAM	
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（C 08 L 9／00 61／10）		

発明の数　1

（全11頁）

㊿ビードフイラーゴム組成物

㉑特　　願　昭53－127256
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㊼特許請求の範囲

1　天然ゴム、ポリイソプレンゴム、ポリブタジエンゴムまたはスチレン－ブタジエン共重合体ゴム若しくはこれらのブレンドゴム100重量部に対して、40～130重量部のカーボンブラツクと、カーボンブラツク100重量部当り15～45重量部の割合でノボラツク型フエノール系樹脂および／またはノボラツク型変性フエノール系樹脂を加え、更に樹脂用硬化剤を配合したことを特徴とするビードフイラーゴム組成物。

2　特許請求の範囲第1項記載のゴム組成物において、カーボンブラツクがヨウ素吸着量（IA）が40～130mg/g、ジブチルフタレート吸油量（DBP）が130ml/100g以下であるカーボンブラツクであるビードフイラーゴム組成物。

3　特許請求の範囲第1項記載のゴム組成物において、カーボンブラツクの配合量が、ゴム100重量部に対して60～120重量部であるビードフイラーゴム組成物。

4　特許請求の範囲第1項記載のゴム組成物において、ノボラツク型フエノール系樹脂の配合量がカーボンブラツク100重量部当り20～40重量部であるビードフイラーゴム組成物。

5　特許請求の範囲第1項記載のゴム組成物において、ノボラツク型フエノール系樹脂がノボラツク型フエノール樹脂、ノボラツク型クレゾール樹脂、ノボラツク型レゾルシン樹脂であるビードフイラーゴム組成物。

6　特許請求の範囲第1項記載のゴム組成物において、ノボラツク型変性フエノール系樹脂が、ロジン油、トール油、カシユー油、リノール酸、オレイン酸、リノレイン酸等のオイルで変性したノボラツク型フエノール系樹脂、キシレン、メシチレン等の芳香族炭化水素で変性したノボラツク型フエノール系樹脂、ニトリルゴム等のゴムで変性したノボラツク型フエノール系樹脂であるビードフイラーゴム組成物。

7　特許請求の範囲第1項記載のゴム組成物において、ノボラツク型フエノール系樹脂とノボラツク型変性フエノール系樹脂の混合割合が80／20～20／80であるビードフイラーゴム組成物。

発明の詳細な説明

本発明はゴム組成物、詳しくはノボラツク型フエノール系樹脂とカーボンブラツクを併用して配合することによつて、特にタイヤのビードフイラーゴムに好適に使用される超硬質のゴム組成物に関する。

ラジアルタイヤのビード部構造はタイヤとして要求される剛性と耐久性を満足させるべく種々の検討がなされており、例えばビード補強層をビード部に配置することによつてタイヤの運動性能、耐久性能等を改善させる試みがなされているが、

このようなものは製造工数が多くなり生産性が著しく劣るといつた欠点を有していた。

一方、超硬質のゴムをビード部に配設することによつて運動性能等を改善することは、実公昭47－16084号公報、フランス国特許第1,260,138号明細書、米国特許第4,067,373号明細書等によりよく知られていることである。しかしタイヤ走行中の複雑な入力下にあるビードフイラーゴムとしての機能を十分に発揮させ、その上でタイヤとして必要な耐久性等についてはとんど考慮されていないのが現状である。

他方、硬質ゴム組成物としては、ノボラツク型フエノール系樹脂を使用することは以前からよく知られているが、それは樹脂と相溶性の良いニトリルゴムやネオプレンゴムについてのものがほとんどで、このようなニトリルゴムやネオプレンゴム系の硬質ゴムをタイヤ部材として使用するには、従来からタイヤ用ゴムとしてよく使用されている天然ゴム、ポリブタジエンゴム等との共加硫性が著しく劣るため、セパレーシヨン等を生じ易く実用に供し得ない。

上記欠点を解決するため本発明者らは天然ゴムやポリブタジエンゴム等にノボラツク型フエノール系樹脂を配合して超硬ゴム組成物を得んとして種々研究したところ、天然ゴム等とノボラツク型フエノール系樹脂は本質的に非相溶であり、通常のゴム製造で行なわれているゴム混練り手法ではノボラツク型フエノール系樹脂は球状の凝集体となつてしまい、単なる充填効果しか示さず、このことはゴムとの相溶性を高めるために各種の変性樹脂を用いたとしても大差はない。しかしながら上記の天然ゴム等とノボラツク型フエノール系樹脂の系にカーボンブラツクを併用するとその併用比により、ゴムと樹脂系による補強効果あるいはゴムとカーボンブラツク系による補強効果とは全く異質の補強効果が現われ、従来の樹脂補強ゴムには見られなかつた極めて耐久性に優れた超硬ゴム組成物が得られることを確かめた。すなわち本来互に非相溶で海島状の大きな相分離状態となる天然ゴムや他のジエン系ゴムとノボラツク型フエノール系樹脂との混合系にカーボンブラツクを併用していくと、ゴム中で樹脂は大きな相分離状態から通常のゴムとカーボンブラツク系にみられる様なカーボンブラツクの分散状態に近い領域まで均質に分散されるようになり、このカーボンブラツクの樹脂に対する相互作用はカーボンブラツクと樹脂の併用比あるいはカーボンブラツクの種類によつても大きく影響を受けることを見出し本発明を達成するに至つた。

従つて本発明は、天然ゴム、ポリイソプレンゴム、ポリブタジエンゴムまたはスチレン－ブタジエン共重合体ゴム若しくはこれらのブレンドゴム100重量部に対して、40～130重量部のカーボンブラツクと、カーボンブラツク100重量部当り15～45重量部の割合でノボラツク型フエノール系樹脂および／またはノボラツク型変性フエノール系樹脂を加え、更に樹脂用硬化剤を配合したビードフイラーゴム組成物に関する。

本発明において使用するゴムは上記の如く天然ゴム、ポリイソプレンゴム、ポリブタジエンゴム、またはスチレン－ブタジエン共重合体ゴム若しくはこれらのブレンドゴムで、かかるゴム100重量部に対してカーボンブラツクを40～130重量部好ましくは60～120重量部、更に好ましくは65～85重量部配合する。カーボンブラツクが40重量部以下では、補強効果を与えるのに必要な量の樹脂を均一に分散させるには少なすぎ、130重量部以上ではゴムが脆くなりゴム組成物の耐久性が極端に悪化するため好ましくない。更に本発明ではカーボンブラツクとしてASTMD1765に規定するヨウ素吸着量（IA）が40～130mg／g、ジブチルフタレート吸油量（DBP）が130ml／100g以下のカーボンブラツクであればより好適である。IAが40mg／g以下では樹脂の分散性に悪影響を与え、130ml／100g以上ではカーボンブラツク自体の分散性が劣るため好ましくない。またDBPが130ml／100g以上では、樹脂を分散させるために必要なカーボンブラツク量において、カーボンブラツクの分散性が悪化してしまう。

本発明の組成物においては、上記カーボンブラツクに、ノボラツク型フエノール系樹脂および／またはノボラツク型変性フエノール系樹脂を併用するが、ノボラツク型フエノール系樹脂とは、ノボラツク型フエノール樹脂、ノボラツク型クレゾール樹脂、ノボラツク型レゾルシン樹脂であり、ノボラツク型変性フエノール系樹脂とは前記のノボラツク型フエノール系樹脂を、ロジン油、トー

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ル油、カシユー油、リノール酸、オレイン酸、リノレイン酸等のオイルで変性した樹脂、キシレン、メシチレン等の芳香族炭化水素で変性した樹脂、ニトリルゴム等のゴムで変性した樹脂である。そしてこれらの樹脂はカーボンブラツク100重量部当り15～45重量部、好ましくは20～40重量部をゴムに加える。樹脂の添加量が15重量部以下では樹脂を添加した効果がほとんどなく補強効果は期待できず、45重量部以上では過剰の樹脂が凝集体を形成し相分離を起こし、ゴム組成物の物性を著しく低下させるため好ましくない。また本発明においては後述の実施例で説明するようにノボラツク型フエノール系樹脂とノボラツク型変性フエノール系樹脂を併用することによつて各々単独で使用した場合に比較して、添加したゴムの耐久性が相乗的に向上するため、このように併用して用いることが好ましい。この場合、ノボラツク型フエノール系樹脂とノボラツク型変性フエノール系樹脂、好ましくはノボラツク型フエノール樹脂とノボラツク型カシユー変性フエノール樹脂あるいはノボラツク型トール油変性フエノール樹脂を併用した時の混合割合は重量比で80／20～20／80、更に好ましくは60／40～40／60である。

本発明において、樹脂用硬化剤とはアルデヒド供与体であるヘキサメチレンテトラミン、パラホルムアルデヒド、ヘキサメトキシメチルメラミン等のホルムアルデヒド発生剤が好適で、樹脂を硬化させるのに必要な量を配合することができる。

本発明においては、前記以外にも硫黄、N，N′－ジチオジアミン類やチウラム類等の加硫剤、加硫促進剤、老化防止剤、カーボンブラツク以外の例えばシリカ等の充填剤、プロセスオイル等を添加しても良い。

以下実施例により本発明を更に詳しく説明する。

実施例　1

第1表に示す配合内容（重量部）により、混練りした各種ゴム組成物をプレス中にて145℃で40分間加硫して、厚さ2㎜の加硫ゴムシートを作成した。このゴムシートを用いて破断時の伸び（Eb）、20％モジユラスおよび動的弾性率を測定した。結果を第1表に示す。尚、Ebと20％モジユラスについてはASTMD 412に準じASTM F型ダンベルにて測定した。また動的弾性率については岩本製作所製ハイパワースペクトロメーターを用い、室温にて長さ25㎜、幅5㎜、厚さ2㎜の短冊状サンプルに、静的に5％伸長させた状態で、周波数10Hz、動歪2％で振動させて測定した。

第1表より明らかな如く、樹脂とカーボンブラツクを本発明の併用比にて配合したゴム組成物は20％モジユラスおよび動的弾性率が著しく向上し、破断伸びにおいても実用上満足される値を有している。

次いでタイヤの軽量化や乗心地性能を向上させるために、第1図に示すようなベルト層2として2プライのスチールコード層とカーカス層3として1500d／2のポリエチレンテレフタレート繊維からなる層の1プライを備えたサイズ165SR13のタイヤ1において、カーカスプライの折返し3′をリムフランジR_Fの近傍の低い位置にとどめた供試タイヤ1のビードフイラー6のゴムとして前記第1表に示す配合№1，№3，№5，№7および№8の各種ゴム組成物を用いて高速走行性、横剛性指数、特殊耐久ドラム試験（A条件、B条件）について検討した。結果を第2表に示す。参考のために、第2図に示すカーカスプライの折返し23′をサイドウオール部25の最大幅付近まで延長した構造を有するタイヤ21のビードフイラー26のゴムとして、前記第1表の配合№1のゴム組成物を用いた従来タイヤについても検討し、結果を合せて第2表に示す。

尚、評価法は次の通りである。

1) 高速走行性

タイヤを4 1/2 Jリムに組み、2.1kg／㎠の内圧を充填し、直径1.7mの金属ドラム上に390kgの荷重で圧着し、80km／hの速度で2時間の慣し走行を行なつた後、3時間放置。次いで121km／hの速度で30分間走行させ異常なく完走すると、8km／h速度を上げ30分間走行させる。同様に完走すると以下8km/h 30分の刻みで連続ステツプアツプし、故障発生時の速度および走行時間を評価した。

2) 横剛性指数

タイヤを4 1/2 Jリムに組み1.7kg／㎠の内圧を充填し、表面に鋸歯状の滑り止めを施した台車上に320kgの垂直荷重で圧着固定し、タイヤの側方向に台車を引張り、タイヤ横変位

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15㎜の時に生じる横荷重を測定し従来タイヤを100として指数で表示した。

3) 乗心地性

路面に高さ10㎜のゴム状突起を固定し、この上を50㎞／hの速度で通過するときの上下方向振動をタイヤ取付軸の反力として加速度計にて測定した。この時記録される波形から第1周期の振幅を当り指数として、従来タイヤ対比の逆数で表示、又、上記の記録波形より減衰係数を求め、従来タイヤ対比の振動の減衰指数として表示した。

4) 特殊耐久ドラム試験（A条件）

タイヤを4 1/2 Jリムに組み、カーカスプライの折返し端部に集中する歪エネルギーが実車通常走行時の約4倍となる様な過荷重、過内圧の条件で直径1.7ｍの金属ドラム上に圧着して60㎞／hの速度で走行させ、カーカスプライ折返し端部に故障が発生するまでの走行距離で示したが30,000㎞まで走行すれば合格とした。

9　10

第 1 表

配合内容 ＼ 配合No.	1	2	3	4	5	6	7	8	9	10
天然ゴム	100	100	100	100	100	100	100	100	50	50
スチレン－ブタジエン共重合体ゴム									50	
ポリブタジエンゴム										50
カーボンブラック *1	70		70	70	70	70	70	100	70	70
ノボラック型カシユー変性フエノール樹脂 *2		20	8	14	20	26	40	30	20	20
ステアリン酸	2	2	2	2	2	2	2	2	2	2
亜鉛華	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5
N－オキシジエチレンベンゾチアゾールスルフエンアミド	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
硫黄	4	4	4	4	4	4	4	4	4	4
ヘキサメチレンテトラミン		2	0.8	1.4	2.0	2.6	4.0	3.0	2.0	2.0
結果										
破断時の伸び、%	170	380	220	230	225	200	100	145	220	190
20%モジユラス、kg／cm²	13.5	7.5	35.0	43.0	60.5	69.0	92.0	89.0	55.0	63.5
動的弾性率、kg／cm²	120	40	350	520	730	890	1530	1420	710	775

*1　IA82mg／g，DBP102ml／100g

*2　フエノール100重量部に対してカシユー油40重量部で変性したノボラツク型フエノール樹脂

第　2　表

タイヤ内容 ＼ タイヤ記号	A	B	C	D	E	F
タイヤ構造	第2図	第1図	第1図	第1図	第1図	第1図
ビードフイラーに使用したゴム配合No.	No.1	No.1	No.3	No.5	No.7	No.8
結果 高速走行性 km/h 分	 185 23	 169 28	 177 27	 185 28	 193 2	 193 4
横剛性指数	100	75	93	103	112	110
乗心地性 当り指数 減衰指数	100 100	115 86	112 93	109 110	105 115	106 113
特殊耐久ドラム試験(A条件)	30,000 km 完走	11,000 km	21,500 km	30,000 km 完走	16,500 km	30,000 km 完走

第2表から明らかなように、本発明のビードフイラーゴム組成物を使用すれば高速走行性、操縦安定性および耐久性が従来タイヤAと同等若しくはそれ以上になり、しかも乗心地性が著しく改善されている。

実施例　2

前記第1表の配合No.5の組成でカーボンブラックのみを第3表に示した各種のカーボンブラックに換えて混練りしたゴム組成物について、ムーニー粘度をJIS K 6300に準じて測定し、更に実施例1と同様に破断時の伸び、20%モジュラス、動的弾性率を求めた。次いでタイヤにおける評価を第1図に示した構造のタイヤで実施例1と同様に行なつた。結果を第3表に示す。

第　3　表

配合内容 ＼ 配合No.	11	12	13	5	15	16	17
カーボンブラック IA mg/g DBP ml/100g	 36 91	 43 121	 86 60	 82 102	 84 150	 121 114	 145 113
結果 ムーニー粘度 破断時の伸び % 20%モジュラス kg/cm² 動的弾性率 kg/cm²	 66 200 38.5 420	 73 220 50.5 610	 85 250 51.5 625	 92 225 60.5 750	 125 200 45.0 595	 105 210 53.0 715	 132 190 42.5 530
タイヤ記号	G	H	I	D		J	
結果 高速走行性 km/h 分	 185 10	 185 21	 185 20	 185 28		 185 20	
横剛性指数	95	97	97	103		98	
特殊耐久ドラム試験 (A条件)	18,000 km	30,000 km 完走	30,000 km 完走	30,000 km 完走		30,000 km 完走	

第3表から明らかな様に、カーボンブラックIAが40～130mg／gで、DBPが130ml／100g以下であれば耐久性が一段と改善されている。尚、配合№15と№17のゴム組成物は、未加硫時の流動性が著しく劣り、押出成型が非常に困難であつたために、タイヤとしての評価は省略した。

実施例　3

第4表および第5表に示した配合内容により混練りした各種ゴム組成物について疲労寿命と他は実施例1と同様に評価した。結果を第4表および第5表に示す。尚、疲労寿命については、ASTMD 412に準じASTM F型ダンベルにて定伸長型疲労試験機を用い温度70℃、伸長率35％に固定し振動を与え、破断するまでの振動数を求めた。

次いでタイヤにおける評価を上記第4表の配合№22～配合№26のゴム組成物および第5表の配合№27，28，30，32，34および36のゴム組成物を使用して第1図に示した構造のタイヤで実施例1と同様に行なつた。但し耐久性については特殊耐久ドラム試験（A条件）に加え、更に過酷な条件、すなわちカーカスプライの折返し端部に集中する歪エネルギーが実車通常走行時の約8倍となる様な超過荷重、超過内圧の条件にてA条件と同様の特殊耐久ドラム試験（B条件）を行なつた。結果を第6表に示す。

第4～6表から明らかなように、無変性のフエノール系樹脂を変性したフエノール系樹脂を併用すると、相乗的にゴム組成物の耐久性が向上している。

第 4 表

配合内容 ＼ 配合№	18	19	20	21	22	23	24	25	26
天然ゴム	100	100	100	100	100	100	100	100	100
カーボンブラツク*1	75	75	75	75	75	75	75	75	75
カシユー変性フエノール樹脂*2	24	18	12	6					
フエノール樹脂*3		6	12	18	24	18	12	6	
トール油変性フエノール樹脂*4						6	12	18	24
ステアリン酸	2	2	2	2	2	2	2	2	2
亜鉛華	10	10	10	10	10	10	10	10	10
N－オキシジエチレンベンゾチアゾールスルフエンアミド	1	1	1	1	1	1	1	1	1
硫黄	6	6	6	6	6	6	6	6	6
ヘキサメチレンテトラミン	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
結果									
破断時の伸び　%	160	160	155	140	120	145	170	165	160
20%モジユラス　kg/cm²	72	70	67	58	52	58	65	66	67
動的弾性率　kg/cm²	980	920	890	715	650	710	780	840	880
疲労寿命　回	2×10^6	3×10^6	5×10^6	4×10^6	3×10^6	6×10^6	8×10^6	4×10^6	1×10^6

*1　IA 82mg／g，DBP 102ml／100g
*2　フエノール100重量部に対してカシユー油40重量部で変性したノボラツク型フエノール樹脂
*3　無変性のノボラツク型フエノール樹脂
*4　フエノール100重量部に対してトール油60重量部で変性したノボラツク型フエノール樹脂

第　5　表

配合内容 ＼ 配合No.	27	28	29	30	31	32	33	34	35	36
天然ゴム	100	100	100	100	100	100	100	100	100	100
カーボンブラツク	75	75	75	75	75	75	75	75	75	75
フエノール樹脂　＊1			18	12	6		18	12	6	
クレゾール樹脂　＊2	24									
レゾルシン樹脂　＊3		24								
芳香族炭化水素変性フエノール樹脂＊4			6	12	18	24				
ゴム変性フエノール樹脂＊5							6	12	18	24
ステアリン酸	2	2	2	2	2	2	2	2	2	2
亜鉛華	10	10	10	10	10	10	10	10	10	10
N－オキシジエチレンベンゾチアゾールスルフエンアミド	1	1	1	1	1	1	1	1	1	1
硫黄	6	6	5	6	6	6	6	6	6	6
ヘキサメチレンテトラミン	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
(結果)破断時の伸び(%)	160	100	130	140	150	160	130	140	150	160
20%モジユラス(kg/cm²)	60	48	58	62	63	60	57	61	62	58
動的弾性率　(kg/cm²)	680	470	740	770	800	750	730	760	765	735
疲労寿命　(回)	2×10^6	4×10^6	4×10^6	6×10^6	5×10^6	4×10^6	4×10^6	6×10^6	5×10^6	4×10^6

＊1　無変性のノボラツク型フエノール樹脂

＊2　無変性のノボラツク型クレゾール樹脂

＊3　無変性のノボラツク型レゾルシン樹脂

＊4　トルエン変性ノボラツク型フエノール樹脂

＊5　ニトリルゴム変性ノボラツク型フエノール樹脂

第 6 表

タイヤ記号 タイヤ内容	K	L	M	N	O	P
ビードフイラーに使用したゴム配合№	№22	№23	№24	№25	№26	№27
高速走行性 km/h 分	185 12	185 21	185 28	185 27	185 28	185 20
横剛性指数	98	101	105	106	106	101
特殊耐久ドラム試験（A条件）	30,000km 完走	30,000km 完走	30,000km 完走	30,000km 完走	30,000km 完走	30,000km 完走
特殊耐久ドラム試験（B条件）	9,800km ゴム破壊	13,000km 完走	13,000km 完走	13,000km 完走	13,000km ゴム破壊	11,000km ゴム破壊

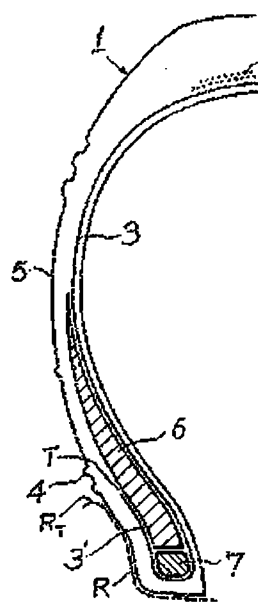
タイヤ記号 タイヤ内容	Q	R	S	T	U
ビードフイラーに使用したゴム配合№	№28	№30	№32	№34	№36
高速走行性 km/h 分	177 26	185 18	185 25	185 20	185 15
横剛性指数	96	103	101	102	99
特殊耐久ドラム試験（A条件）	28,000km ゴム破壊	30,000km 完走	30,000km 完走	30,000km 完走	30,000km 完走
特殊耐久ドラム試験（B条件）	6,700km ゴム破壊	13,000km 完走	12,000km ゴム破壊	13,000km 完走	11,500km ゴム破壊

図面の簡単な説明

第1図は本発明のビードフイラーゴム組成物を使用したタイヤの性能評価に利用したタイヤの側方部分断面図、第2図は従来タイヤの側方部分断面図である。

1，21……タイヤ、2，22……ベルト層、3，23……カーカス層、3′，23′……カーカスプライの折返し、4，24……ビード部、5，25……サイドウオール部、6，26……ビードフイラー、7，27……ビードワイヤー、28……コード層、R……リム、R_T……リムフランジ。

第1図



第2図